Phase Equilibria and Properties of Dielectric Ceramics

Ceramic compounds with exploitable dielectric properties are widely used in technical applications such as actuators, transducers, and resonators or filters for wireless communications. The commercial competitiveness of next-generation devices depends on new ceramics with improved properties and/or reduced processing costs. Experimental phase equilibria determination, integrated with systematic chemistry-structure-property studies (experimental, theoretical, and modeling) contribute toward the fundamental understanding and rational design of these technologically important materials.

Terrell A. Vanderah, Benjamin P. Burton, Eric J. Cockayne, and Igor Levin

Ternary oxides in the Bi_2O_3-ZnO-Nb_2O_5 system exhibit high-dielectric constants (ε), relatively low dielectric losses, and compositionally tunable temperature coefficients of capacitance (τ_c). Such properties combined with sintering temperatures of less than 950ºC render these materials attractive candidates for capacitor and high-frequency filter applications in multilayer structures co-fired with silver electrodes. The system features two structurally distinct ternary compounds, $Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$ (ε = 145, τ_c = –400 MK^{-1}) and $Bi_2Zn_{2/3}Nb_{4/3}O_7$ (ε = 80, τ_c = +200 MK^{-1}), which exhibit very dissimilar dielectric properties and form temperature-stable, commercially important mixtures. However, the absence of structural information for both phases has precluded understanding of the unusual dielectric properties; in particular, $Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$ ceramics exhibit dielectric relaxation, attributed to a dipolar glass-like mechanism, while no such behavior is observed for $Bi_2Zn_{2/3}Nb_{4/3}O_7$. Recent studies combined electron, x-ray, and neutron powder diffraction techniques to elucidate the crystal structures of these compounds which feature pyrochlore and zirconolite-like structures, respectively. The results reveal that displacive disorder in $Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$ is responsible for the high dielectric constant and the relaxation phenomenon.

Subsolidus phase relations have been determined for the BaO:TiO_2:Ta_2O_5 system and the BaO:Ta_2O_5 subsystem, which are pertinent to the processing of Ta_2O_5-based ceramics for cellular base station resonators and filters. $BaTiO_3$ dissolves a considerable amount of Ta^{5+} by forming Ti^{4+} vacancies. The formation of $Ba_3Ti_4Ta_4O_{21}$, a member of the hexagonal $A_3M_8O_{21}$–type ternary oxides, was confirmed as well as its solid solution. Several new compounds have been found, including four members of the orthorhombic "rutile-slab" homologous series, $BaTi_nTa_4O_{11+2n}$, with n-values 3,5,7,9. Three ternary phases with close-packed [Ba,O] layer structures related to that of *6L* $Ba_4Ti_{13}O_{30}$ were found: *13L* $Ba_{18}Ti_{53}Ta_2O_{129}$, *7L* $Ba_{10}Ti_{27}Ta_2O_{69}$, and *8L* $Ba_6Ti_{14}Ta_2O_{39}$. The crystal structures of the *13L* and *7L* phases were determined by single-crystal x-ray diffraction. Phases with tetragonal tungsten bronze related structures occur over large compositional ranges, both within the ternary and along the BaO-Ta_2O_5 binary.

$PbZr_{1-x}Ti_xO_3$ (PZT) is an important piezoelectric material that has applications in transducers. A first-principles-based effective Hamiltonian was developed for Zr-rich PZT. This model is the first that reproduces the correct sequence of phase transitions in this system: orthorhombic to rhombohedral to cubic, as the temperature increases.

Other important transducer materials include relaxor ferroelectrics. An effective Hamiltonian was developed for the relaxor ferroelectric $PbSc_{1/2}Nb_{1/2}O_3$ (PSN), based on first-principles calculations. This model allows one to simulate the structure and dielectric properties of PSN as a function of cation ordering, temperature, and applied fields, in systems representing as many as 300,000 atoms. Molecular dynamics methods allow the polarization dynamics and frequency dependence of the dielectric permittivity to be studied. The local electric field at the Pb sites due to the charged Sc and Nb ions has been calculated (see Figure 1) and incorporated into the model. The results establish a clear link between chemical disorder and dielectric response, and they indicate "nanoscale texture," i.e., the size and geometrical arrangement of domains play a fundamental role in the observed macroscopic properties.

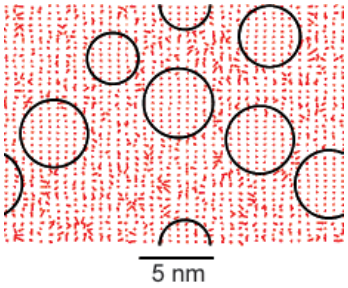

Figure 1: *Local electric fields in a model for the relaxor ferroelectric PSN. Experiments suggest that relaxor ferroelectrics contain chemically-ordered regions in a disordered matrix and that such inhomogeneities may be responsible for the relaxor behavior. Computations show that chemically-ordered regions in PSN (circles) have much lower local fields than the disordered matrix.*

Contributors and Collaborators

R.S. Roth, W. Wong-Ng, J.E. Maslar (CSTL); R. Geyer (EEEL); S. Bell (TRAK Ceramics, Inc.); C.A. Randall (Penn State); J.C. Nino (Penn State); K. Leung (Sandia); L. Bellaiche (University of Arkansas); U. Waghmare (JNCASR, Bangalore, India); S. Prosandeev (Rostov State University, Russia); V. Zelezny and J. Petzelt (Czech Academy of Sciences)